X-ray Scattering at the ALS: An Overview

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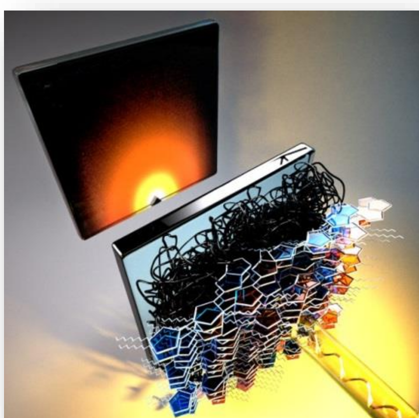
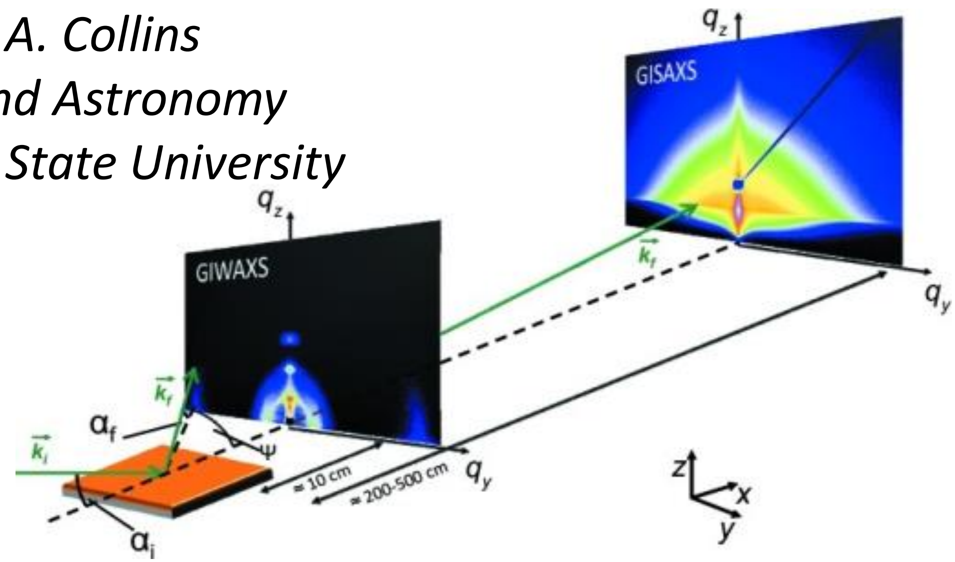


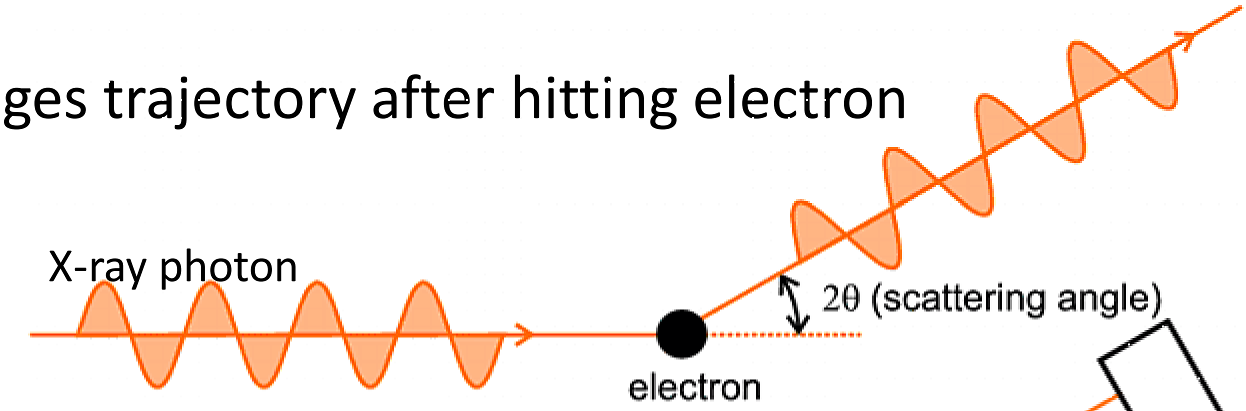


Outline

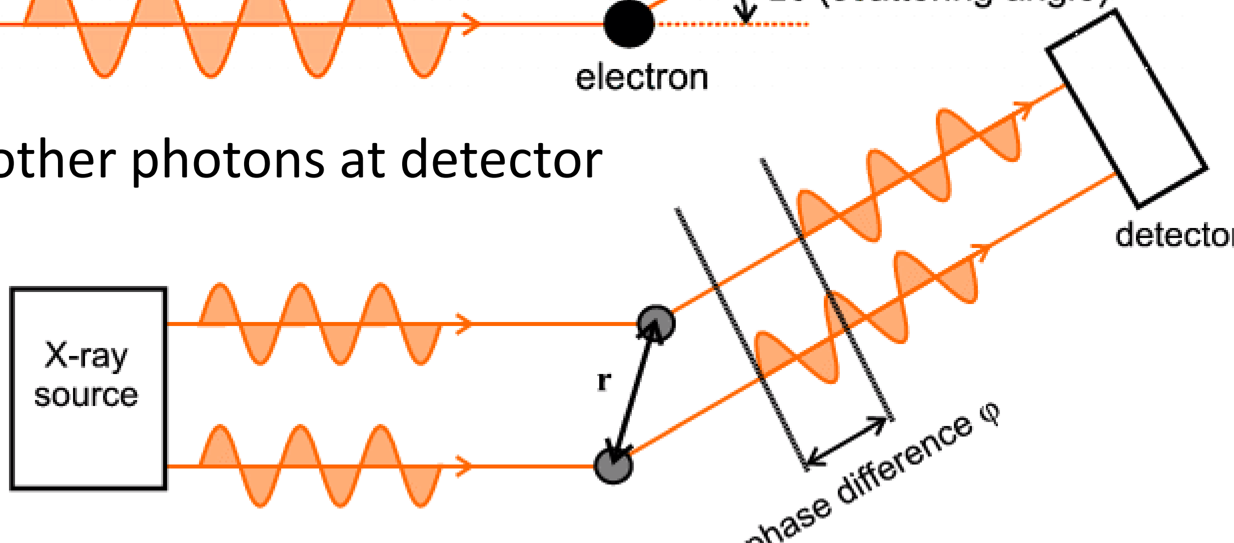
- What is scattering and what does it measure?
- Traditional Elastic Scattering
  - Wide-angle scattering and diffraction
  - Small-angle scattering
  - Reflectivity
- Coherent Scattering Techniques
  - Coherent diffractive imaging (ptychography)
  - X-ray photocorrelation spectroscopy (XPCS)
- Resonant Soft X-ray Scattering
  - Sorting out order in molecular systems

What is X-ray Scattering?

- Photon changes trajectory after hitting electron



- Interferes with other photons at detector

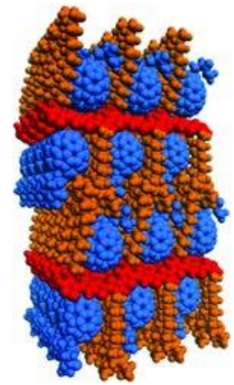


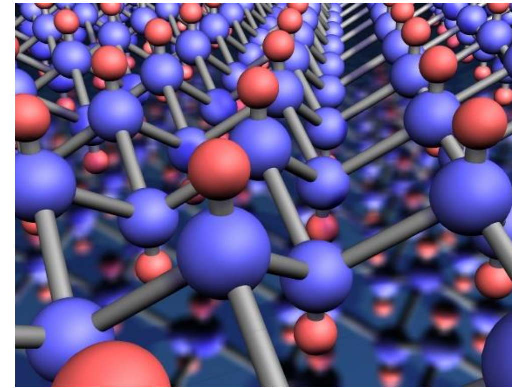
- Intensity vs angle (θ) tells about r (distance) between scatterers

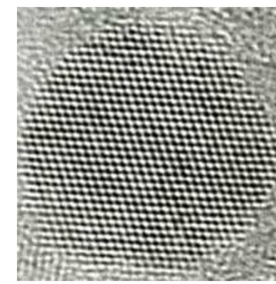
$\Delta\phi$ determines if constructive or destructive interference
E.g. Bragg's Law:
$$2d\sin\theta = m\lambda$$

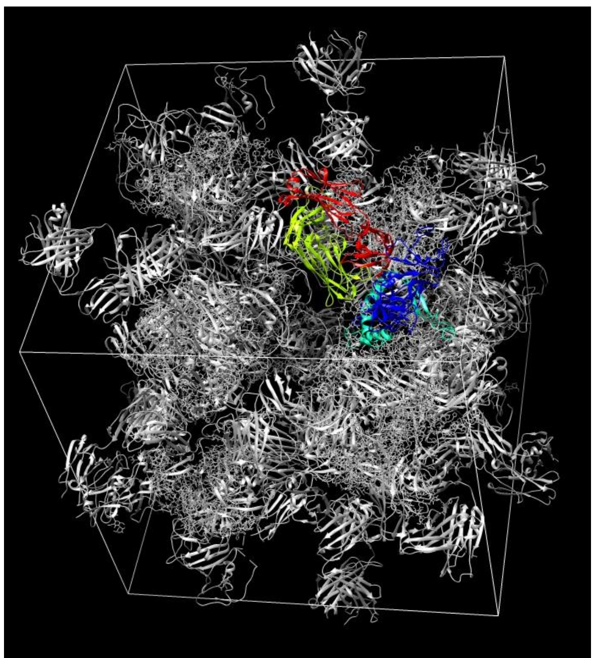
Scattering: Statistics of internal structure

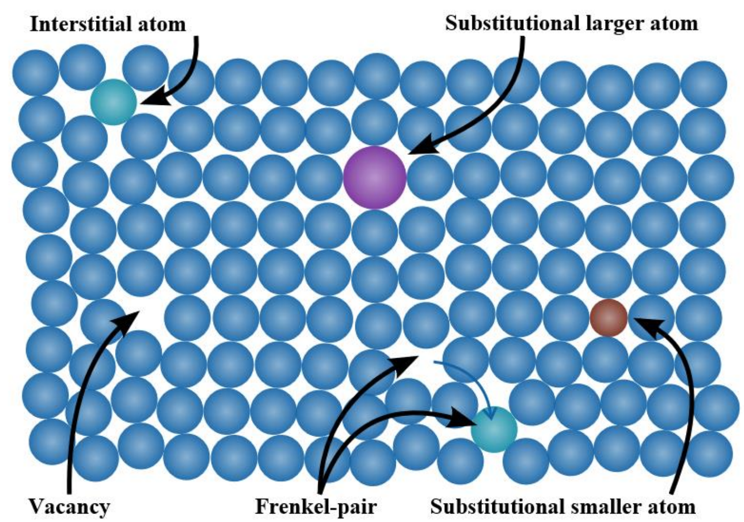
- Crystal atomic spacing, arrangement
  - Strain, defects (faults, disorder)
  - Thin film orientation
  - Grain/crystallite size
  - Macromolecular structure











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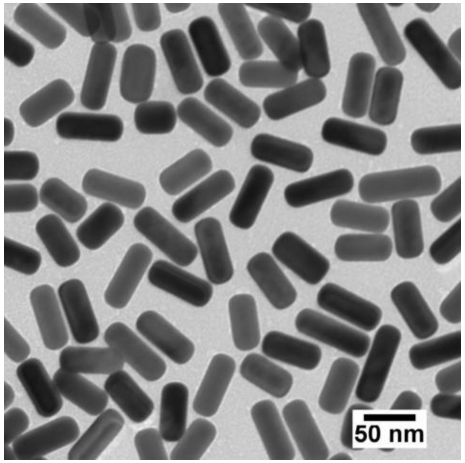
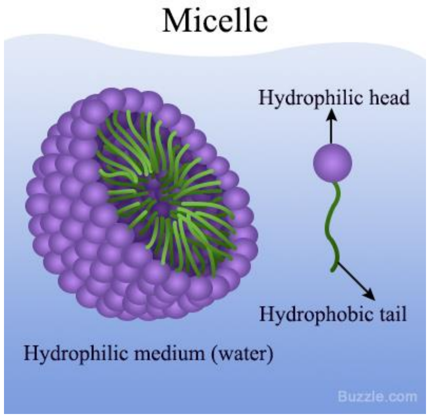
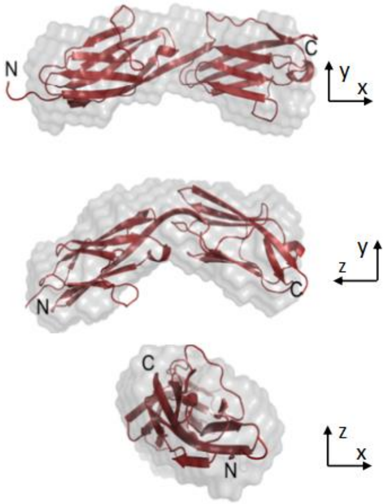
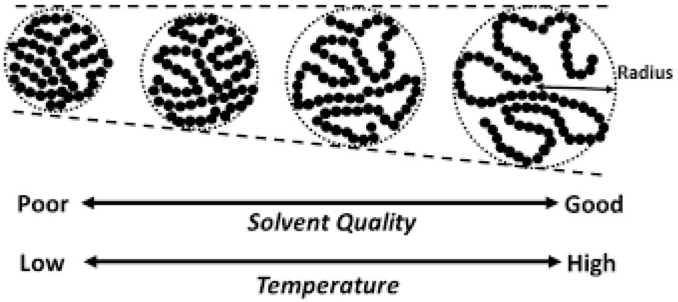
- Nanoparticle size & shape
  - Statistics if disordered
  - Conformation of macromolecules









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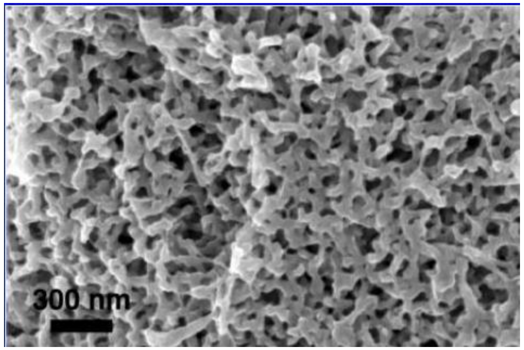
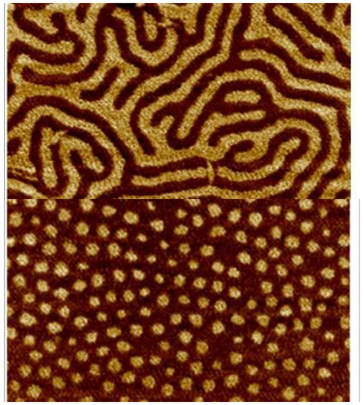
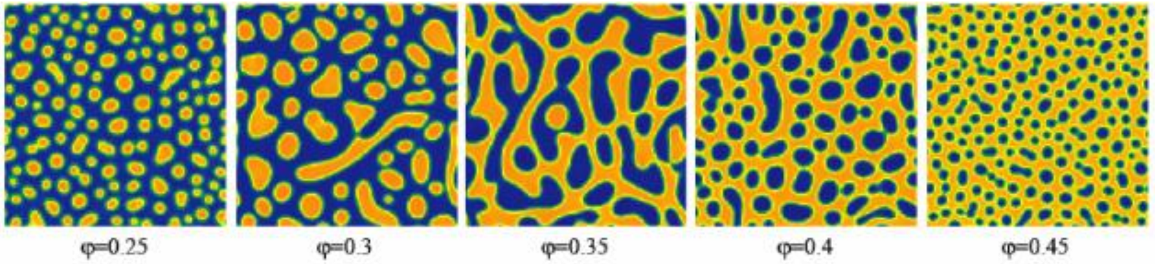
- Nanophase separation/identification
  - Composition, volume fraction
  - Pore size, volume







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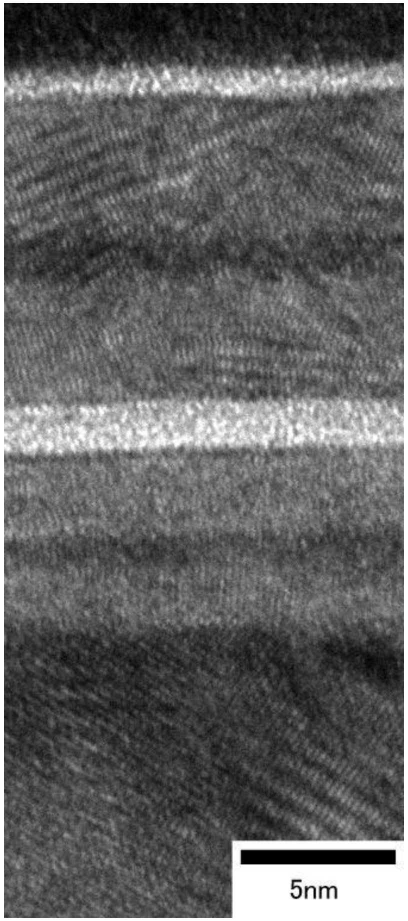
  - Composition, volume fraction
  - Pore size, volume
- Thin film stratification
  - Thickness, roughness

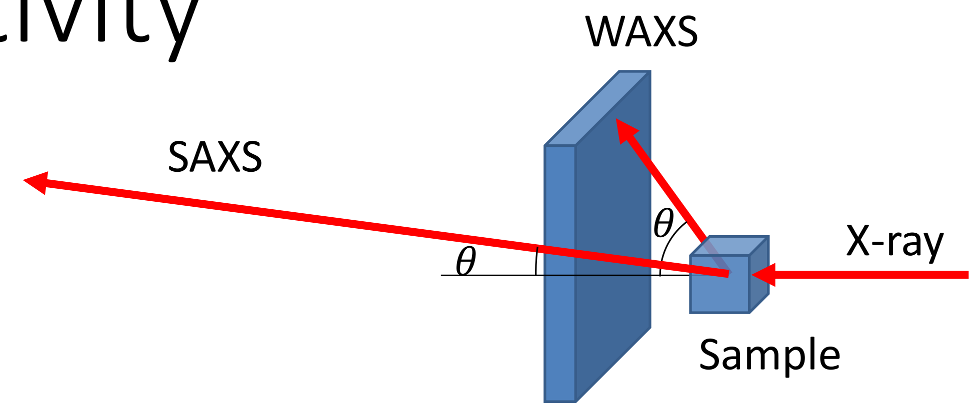
All non-destructive measurements!

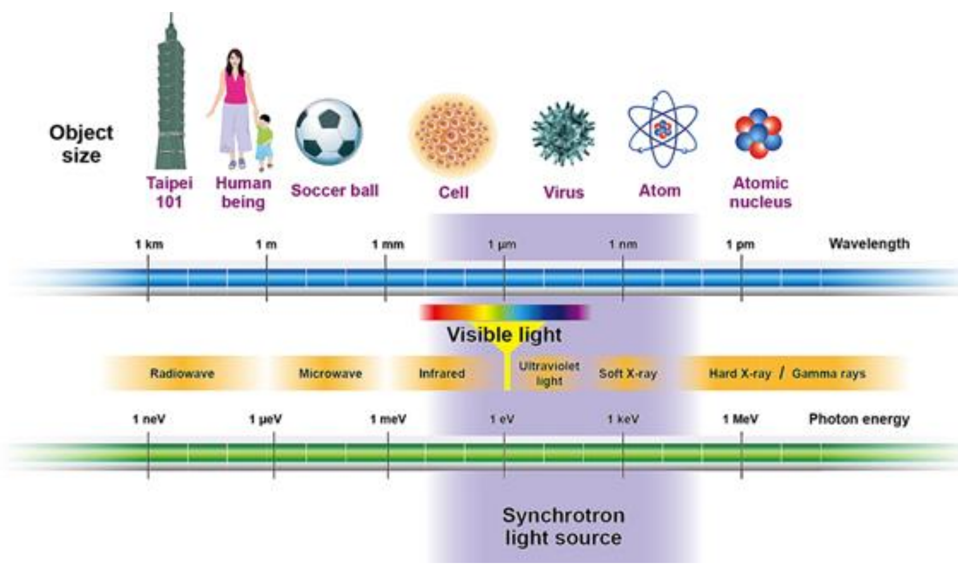


Size Scale Sensitivity

- Bragg Law: $2d \sin\theta = \lambda$
  - $d_{min} \sim \frac{\lambda}{2}$
  - $d_{max} \propto \theta_{min}$

    (beam size/divergence)
- SAXS vs WAXS
  - Switch $\theta \sim 2°$ for hard X-rays (10keV)
  - Accomplished via detector distance





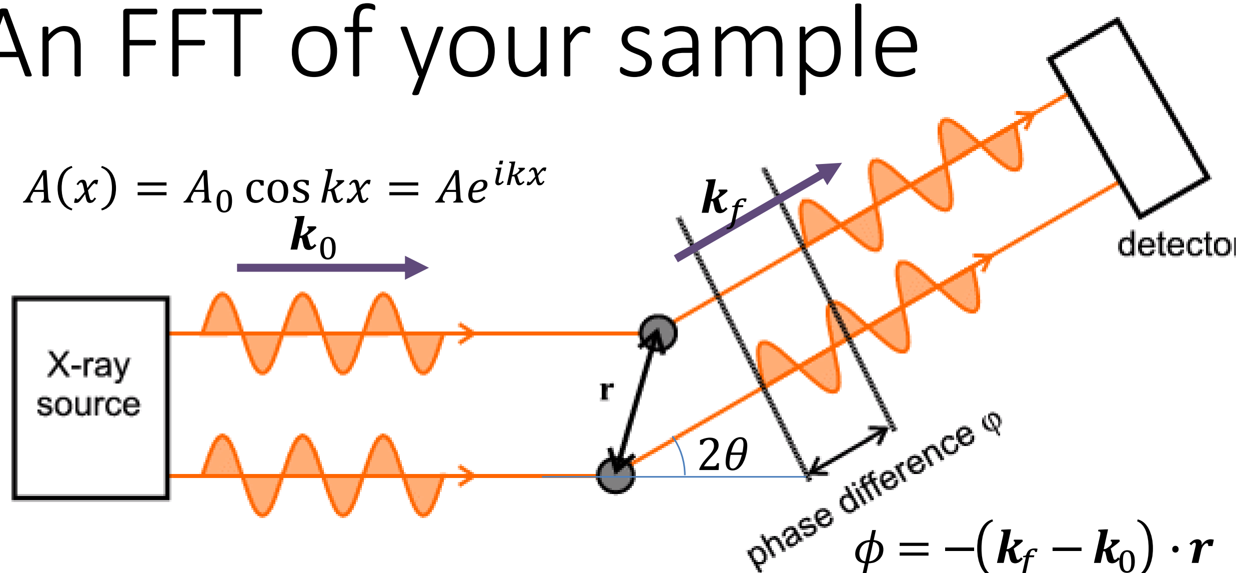
Scattering: An FFT of your sample

Elastic Scattering

$$|k_0| = |k_f| = \frac{2\pi}{\lambda}$$

No energy transfer

$$A(x) = A_0 \cos kx = Ae^{ikx}$$



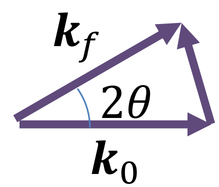
$$\phi = -(\boldsymbol{k}_f - \boldsymbol{k}_0) \cdot \boldsymbol{r}$$
$$= -\Delta \boldsymbol{k} \cdot \boldsymbol{r}$$
$$= -\boldsymbol{q} \cdot \boldsymbol{r}$$

Constructive Interference

$$A_{det}(r) = b_e e^{i\phi}$$

Sum over illuminated sample

$$A_{det}(\boldsymbol{q}) = \int_V \rho_e(\boldsymbol{r}) e^{-i\boldsymbol{q}\cdot\boldsymbol{r}} d\boldsymbol{r}$$



$$\boldsymbol{q} \equiv \Delta \boldsymbol{k}$$

$$q = 2k \sin\theta$$

Fourier Transform of the electron density distribution!

(Just like electron microscopists do, but huge sample)

$\boldsymbol{r}$: 'Real Space'
$\boldsymbol{q}$: 'Reciprocal Space'
Also 'Spatial frequency'
Big $\boldsymbol{q}$ = Small $\boldsymbol{r}$

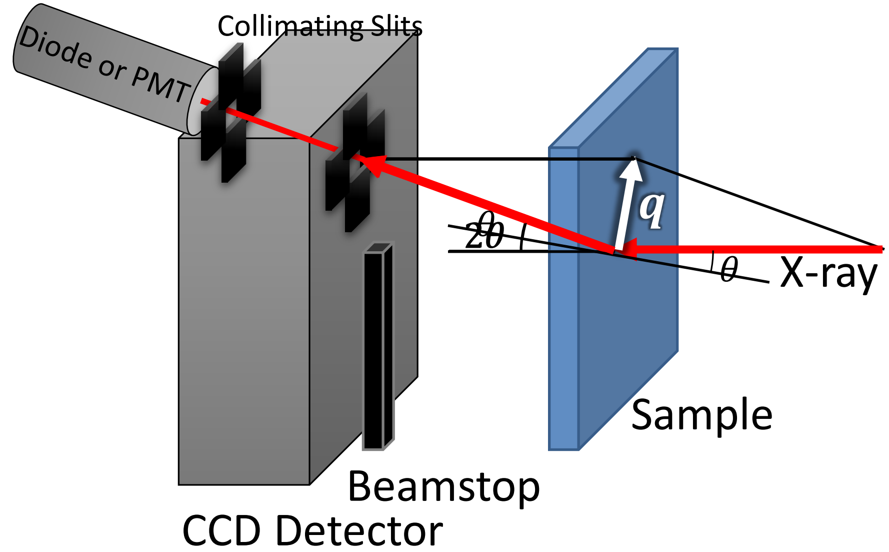
Measure intensity, lose $e^{-i\boldsymbol{q}\cdot\boldsymbol{r}}$

$$I(\boldsymbol{q}) = A(\boldsymbol{q})A^*(\boldsymbol{q})$$

Can't take IFT to recover $\rho_e(\boldsymbol{r})$

...except for COSMIC!!!

Experiment

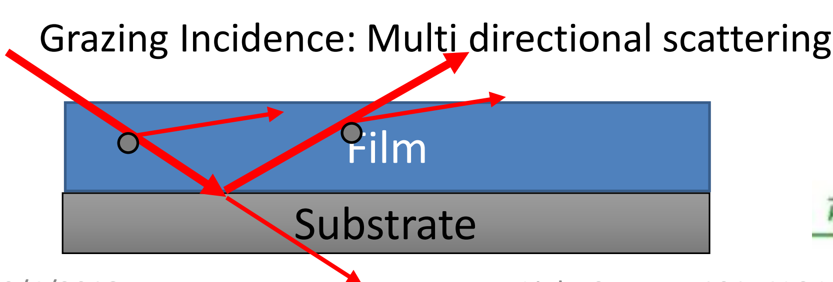


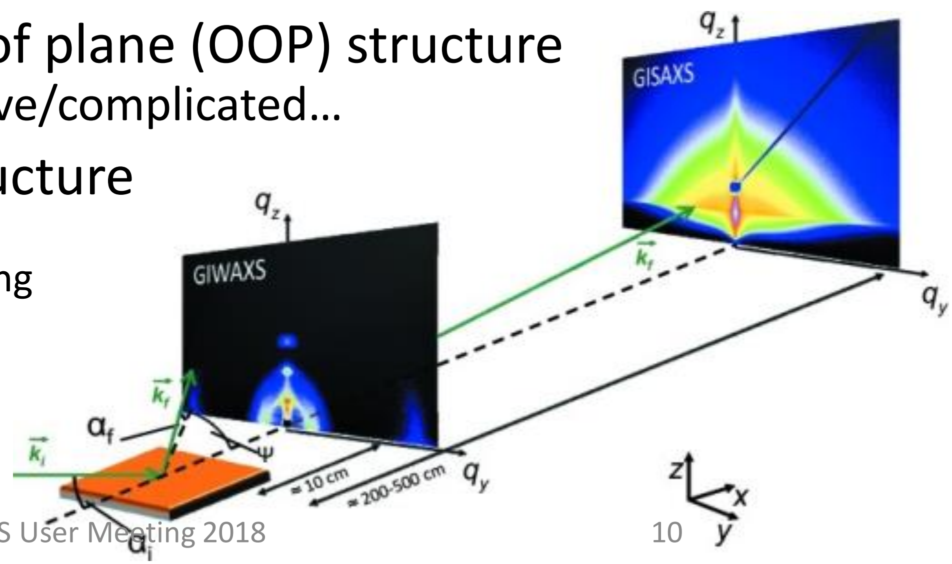
<u>Detectors</u>

- Point Detector: High q-res
  - high crystalline materials
- Area Detector (CCD): speed
  - amorphous, in-situ studies

<u>Sample Geometry</u>

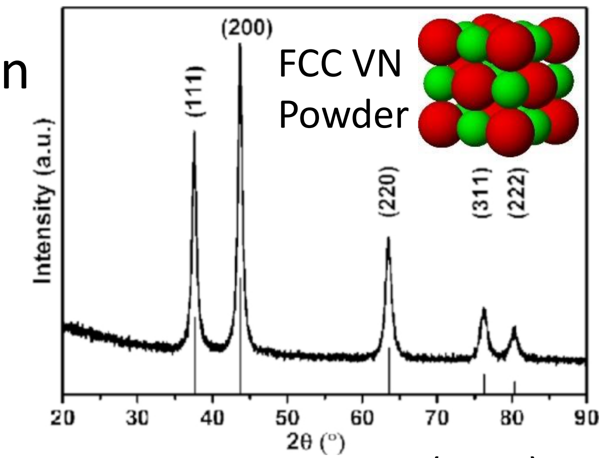
- Transmission: probe mainly in-plane (IP) structure
  - Similar to transmission microscopy (TEM)
- Grazing: Probe both IP and out-of plane (OOP) structure
  - Analysis might be more qualitative/complicated…
- Reflectivity: Probe only OOP structure



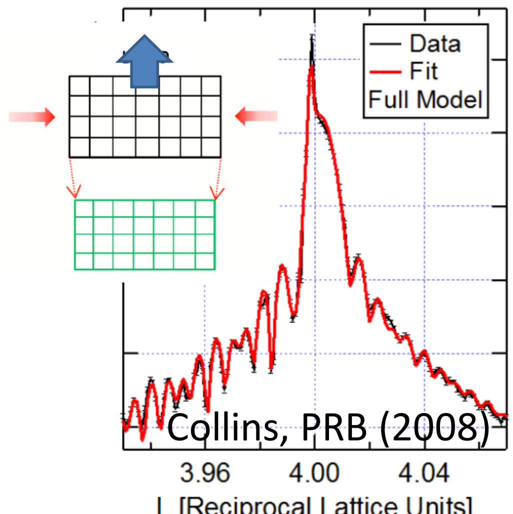


Diffraction modes and their applications

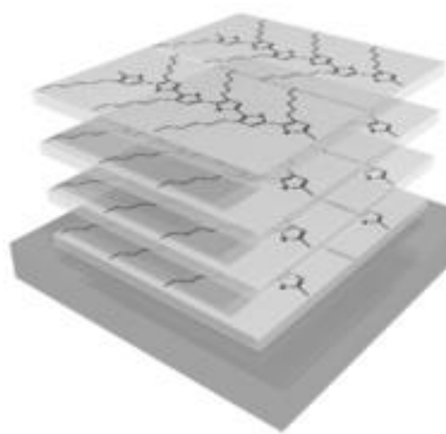
- Powder: isotropic crystal orientations
  - See every diffraction peak in one $I(\theta)$ scan
  - Get Bulk Properties
- Thin film: isotropic IP, but orient OOP
  - Use grazing sample geometry
  - Confinement/interfacial effects
- Single crystal: (point detector)
  - Strain states, defects, atomic effects

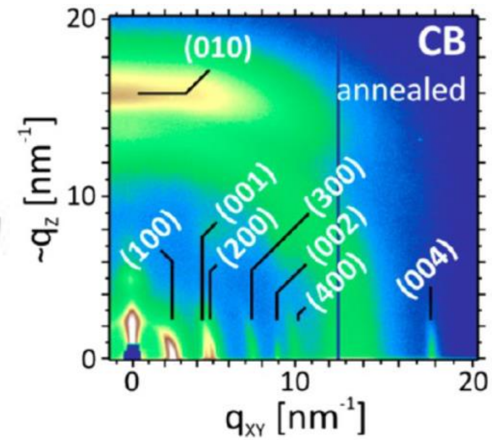


K. Huang, Sci Rep (2015)



Collins, PRB (2008)





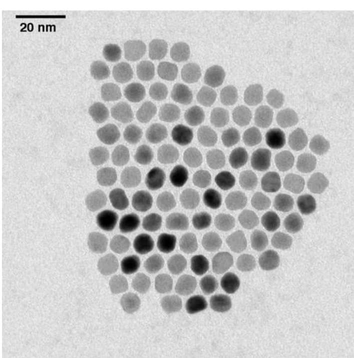
R. Steyrleuthner, JACS (2014)

Peak broadening: Grain size & disorder

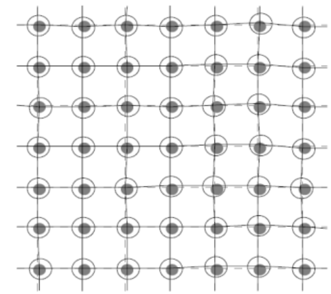
Instrument Resolution
(beam divergence, size, $\Delta\lambda$)

Nanocrystal Size
Coherence Length
Scherrer Analysis

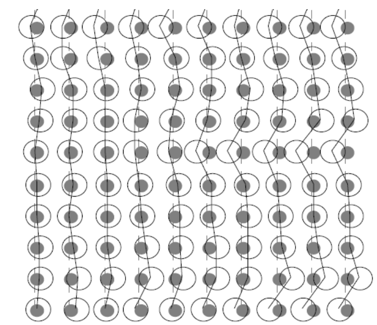
$$D \cong \frac{2\pi K_{shape}}{\Delta q_{FWHM}}$$

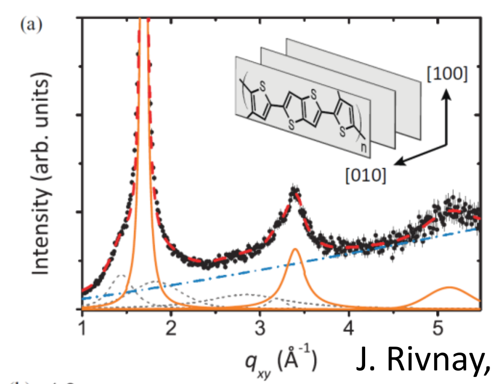


Debye-Waller Disorder
(Thermal, random)
RMS fluctuation around equilibrium positions

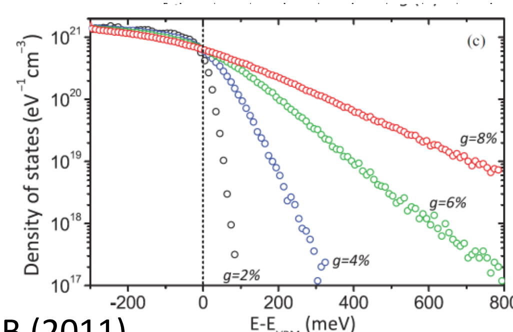


Paracrystalline Disorder
Builds up over unit cells
Warren-Averbach Analysis





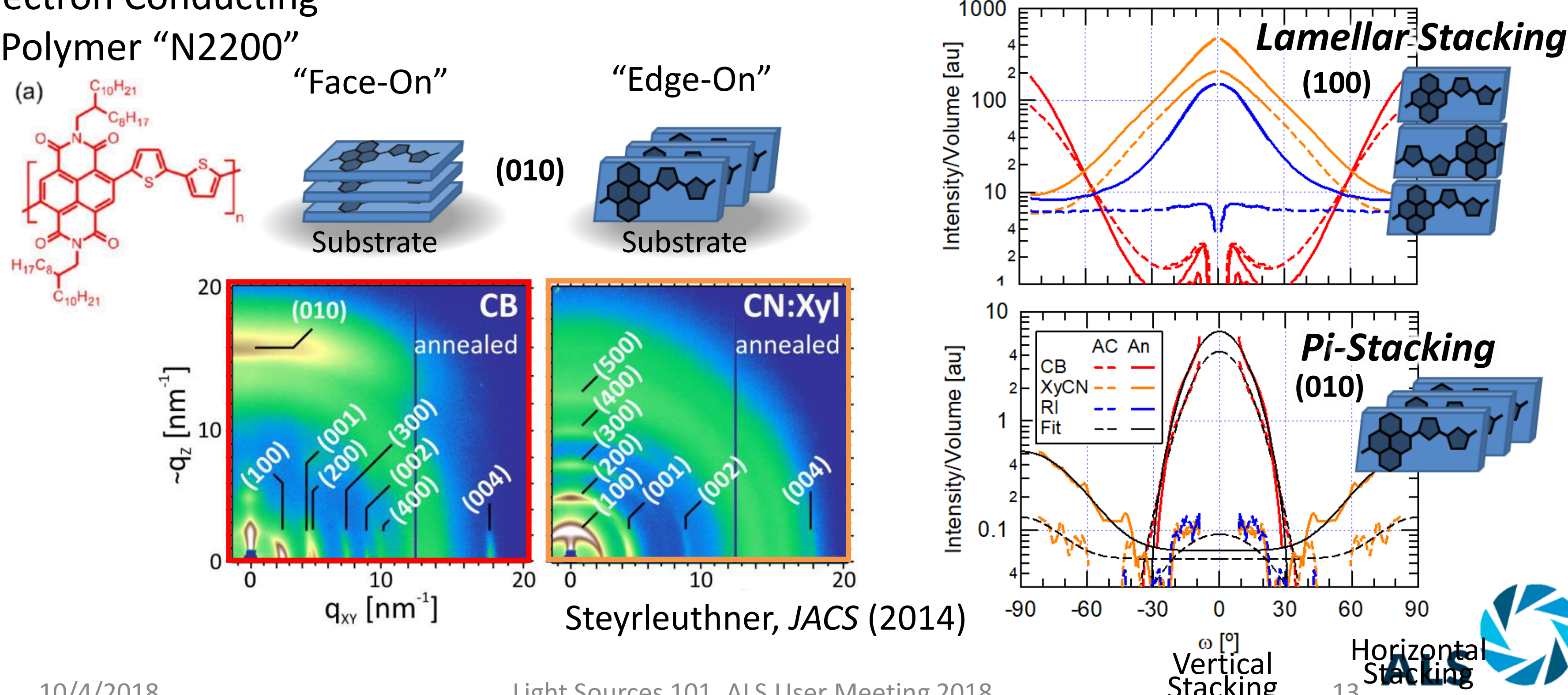
J. Rivnay, PRB (2011)



Crystal orientation in a thin film

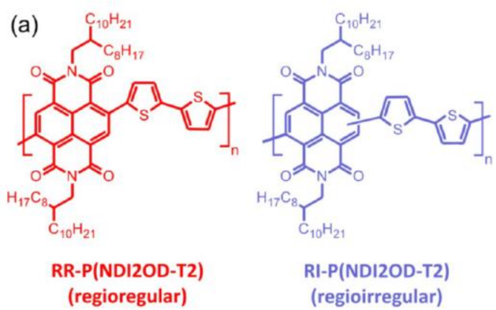
- Interfaces affect crystal orientation distribution in thin films
- Distribution obtained via "**Pole Figure**" from GIWAXS
- Relative **Degree of Crystallinity** from integrating pole figure

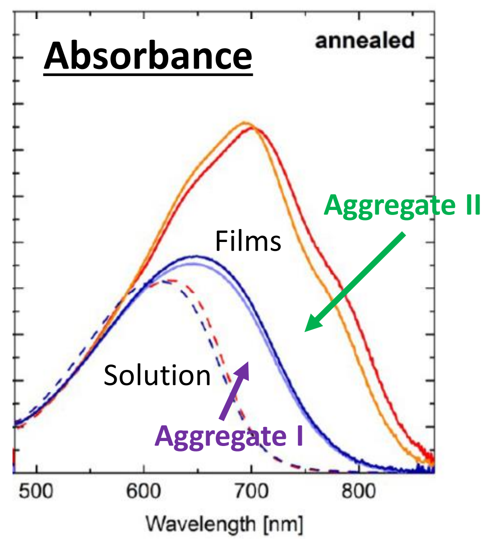
Electron Conducting Polymer "N2200"

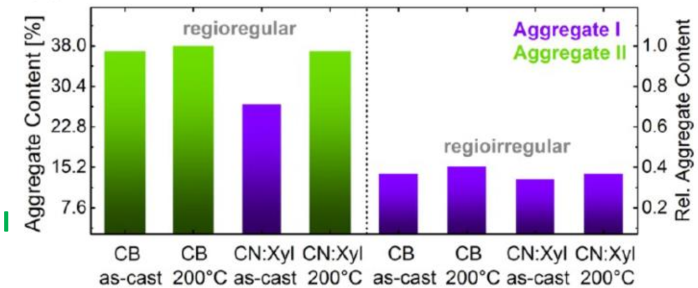


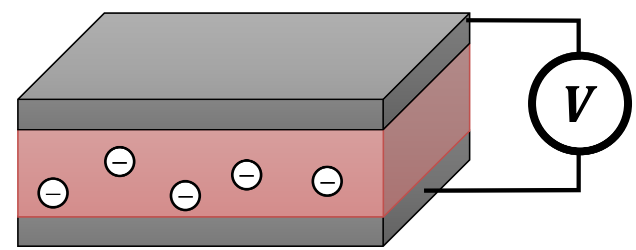
Steyrleuthner, *JACS* (2014)

Aggregation-crystallinity-charge transport in conjugated polymers

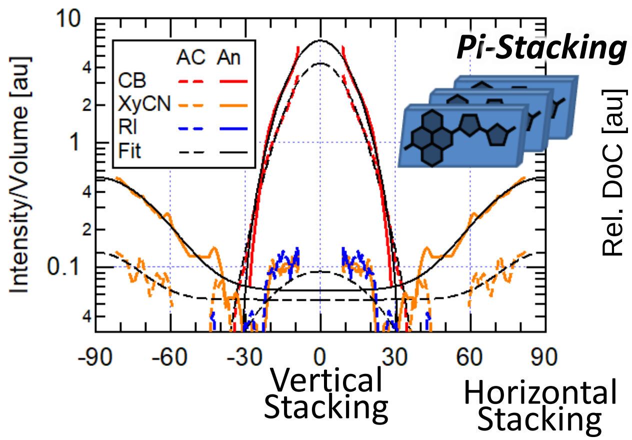


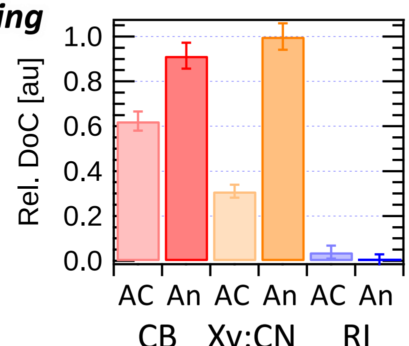




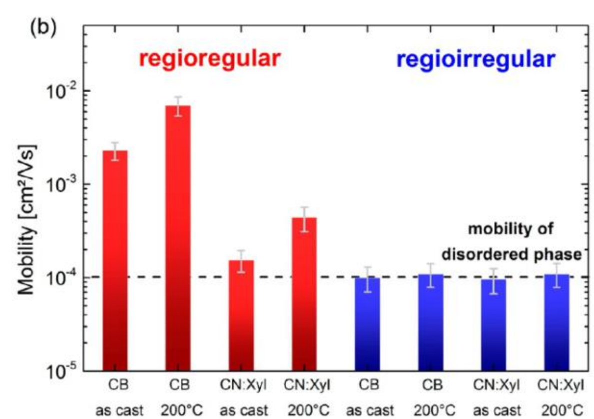


GI-XRD (7.3.3)



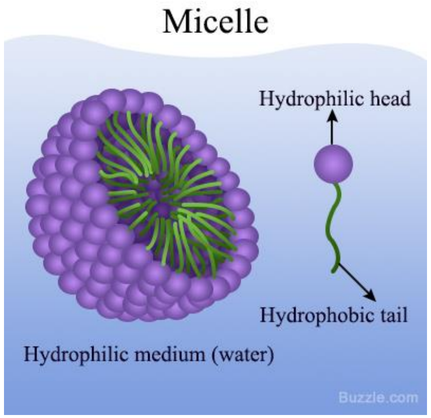


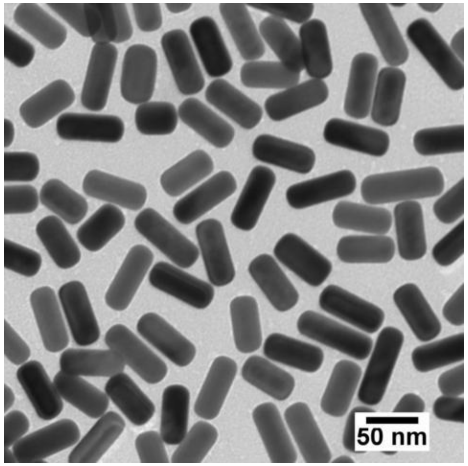
Steyrleuthner, *JACS* (2014)

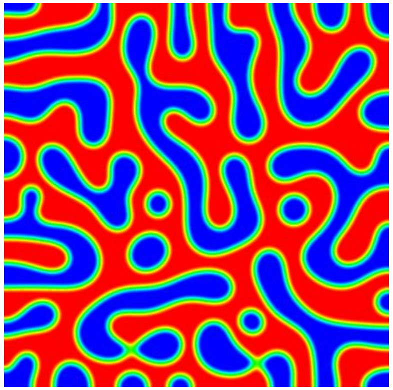


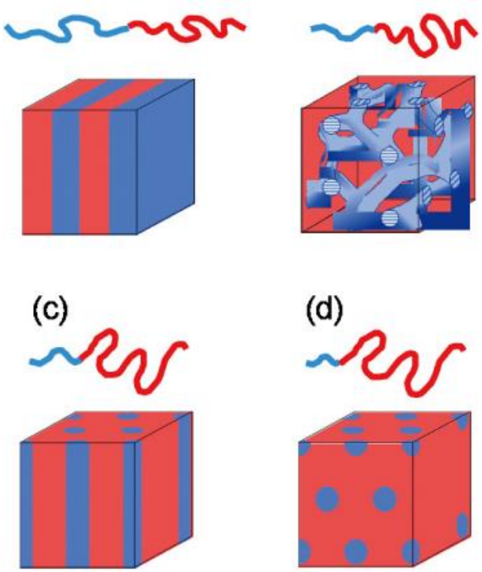
Small angle scattering

- Larger scale than atomic/molecular $D > 1\,nm$
  - Have to be careful of direct beam!
- Dilute particulate systems
  - Scattering within particle gives shape and size
  - Incoherent scattering between particles
- Phase separated structures
  - Mean domain size, interphase boundary
  - Larger periodic structures from macromolecules or biomolecules



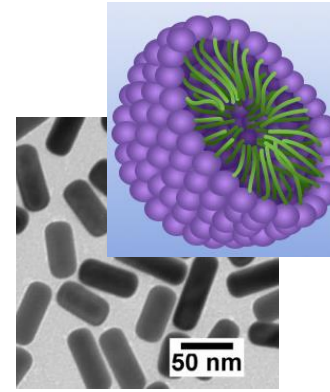




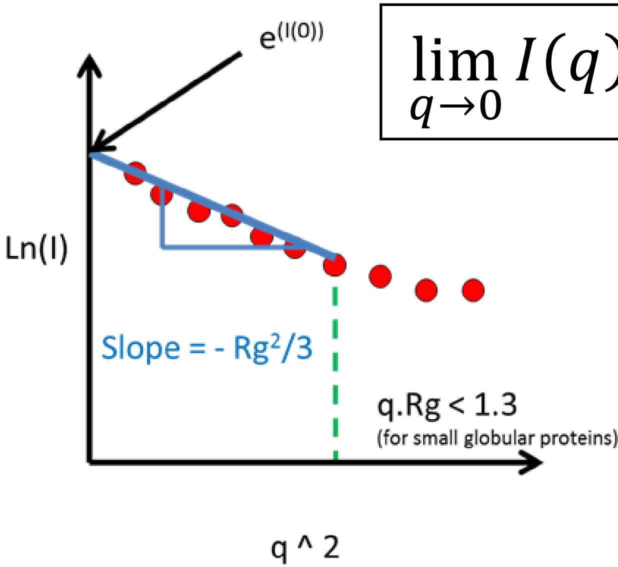


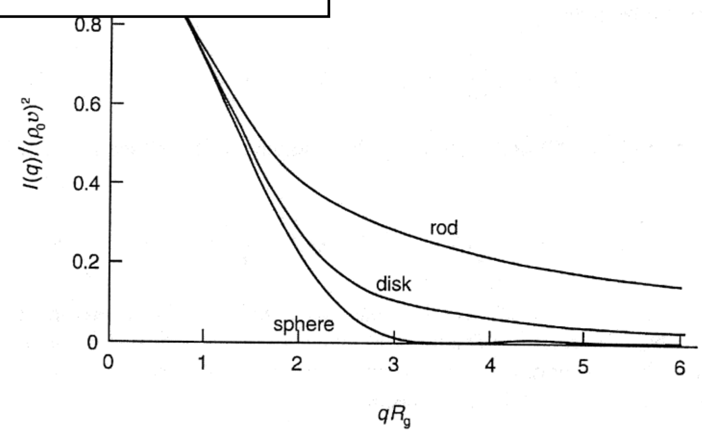
SAS Data Analysis: Dilute Particles

- Simple particle shapes: Get dimension statistics
  - Spheres, Rods, Disks (distribution of radii and length)
  - Assumption: equal probability for all orientations
- Guinier Law: Get size if you don't know the shape
  - Particle "Radius of Gyration" R_g
  - Assumptions: $q \ll 1/R_g$, dilute ($C < 1v.\%$), no other scattering



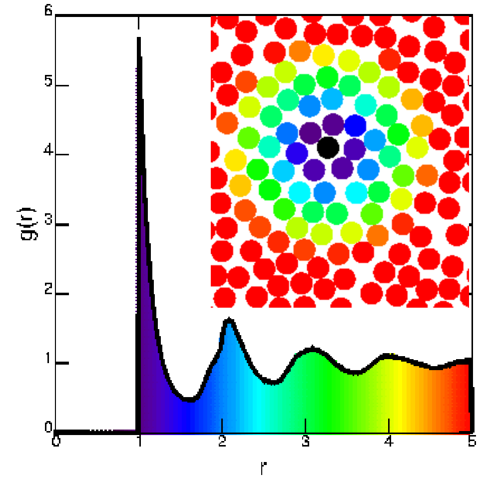
$$\lim_{q \to 0} I(q) = \rho_e^2 v^2 \exp(-\tfrac{1}{3} q^2 R_g^2)$$



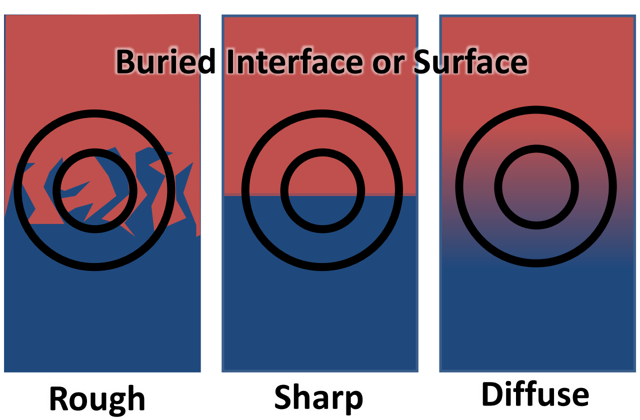


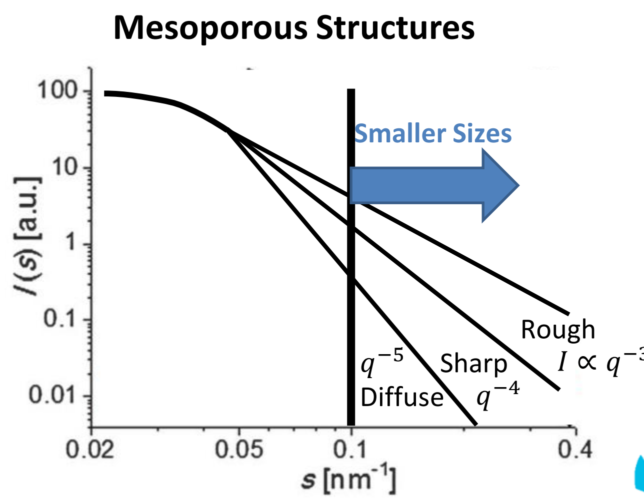
SAS: Two-phase systems

- Auto/Pair Correlation $\Gamma(\boldsymbol{r}) = IFFT[I(\boldsymbol{q})]$
  - Avg length scale of domains (sizes, distances)
- Porod Invariant $Q = \int I(\boldsymbol{q})d\boldsymbol{q} = V\phi_1\phi_2|\Delta\rho_e|^2$
  - Phase volume fractions
  - Domain ‘contrast’ (RMS fluctuations)
- Porod Law $\lim_{q\to\infty} I(q)/Q = \frac{2\pi}{\phi_1\phi_2 q^4}\frac{S}{V}$
  - Specific Interfacial Area
  - Interface roughness/diffusivity



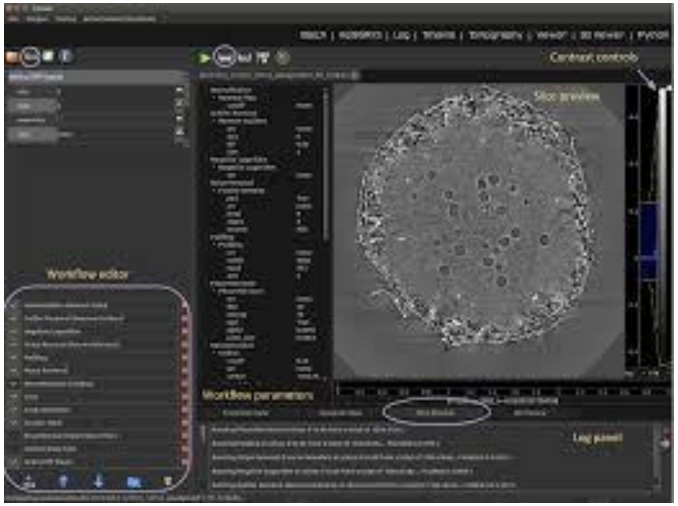
Emory University

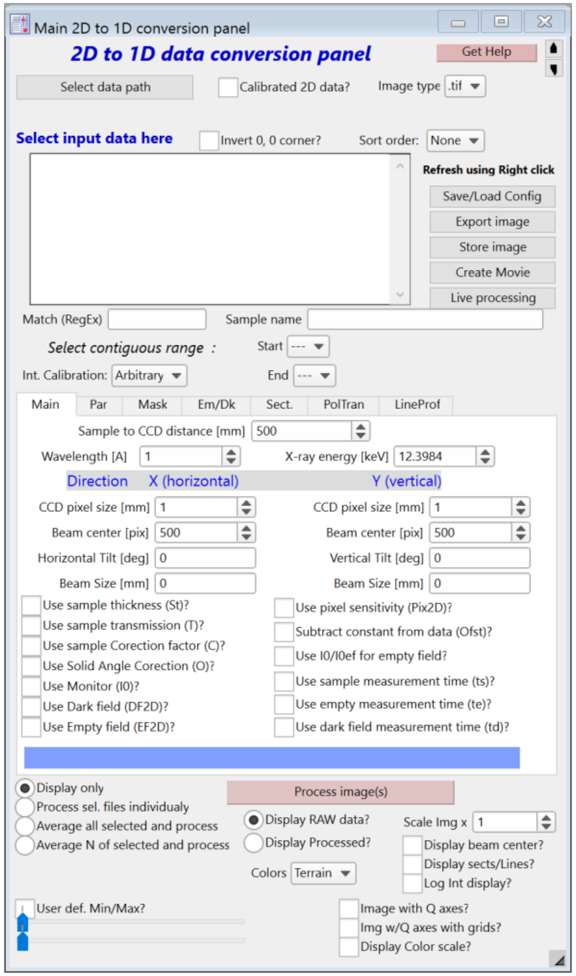




Data Processing

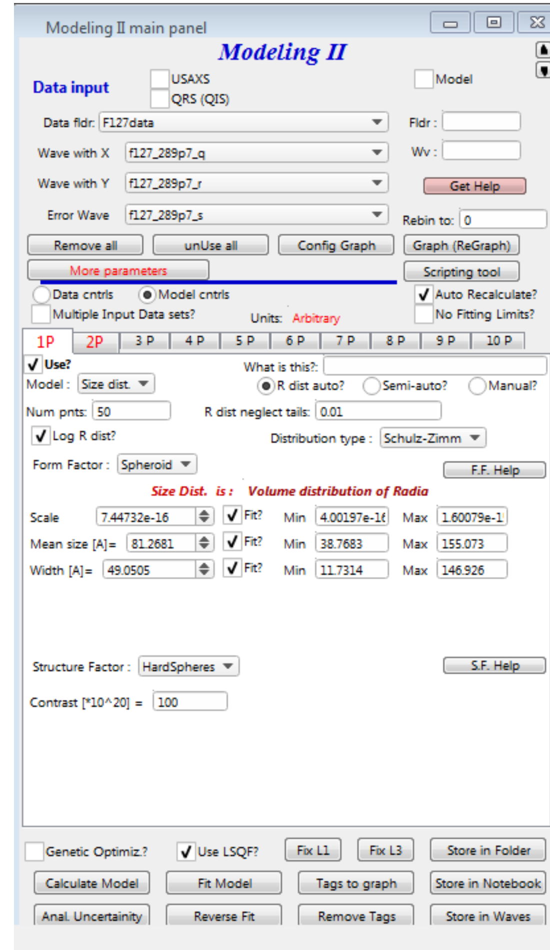
- **NIKA** – processing tool coded by Jan Ilavsky (ANL)
  - Runs in Wavemetics' ***Igor Pro***
  - Converts 2D CCD data into $I(q)$
  - Handles most detectors
- **XICAM** – Next generation processing/analysis tool
  - Python based

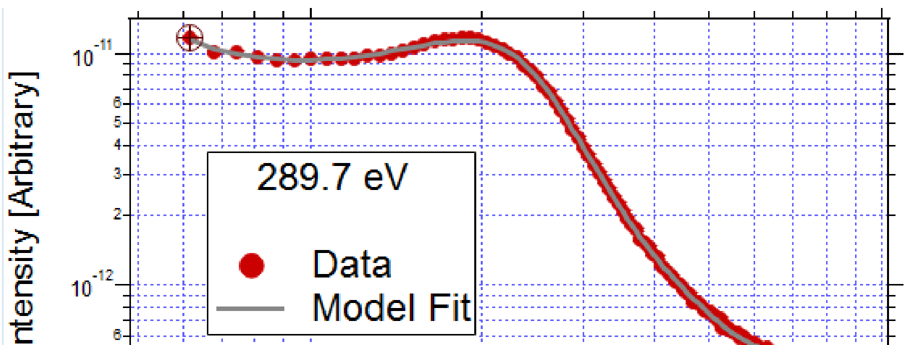




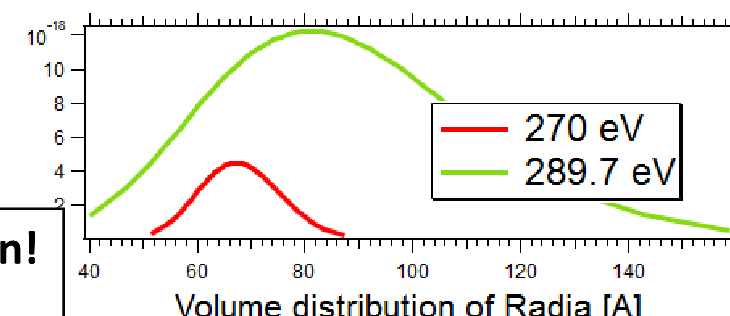
Data Analysis

- **IRENA** –by Jan Ilavsky (ANL) ***Igor Pro***
  - Power Diffraction fitting
  - Particle Modeling
  - Guinier Analysis
- NCNR/NIST SANS Analysis
  - ***Igor Pro***
- Fit2D (ESRF)



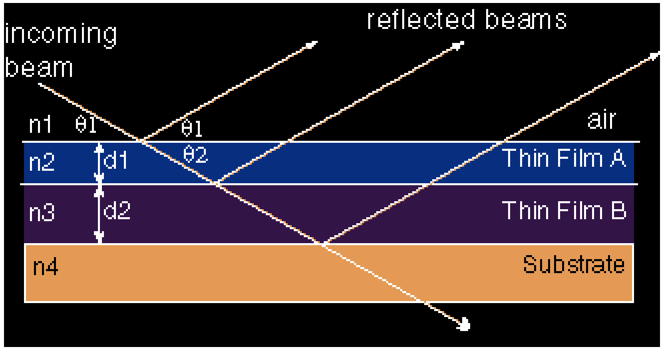


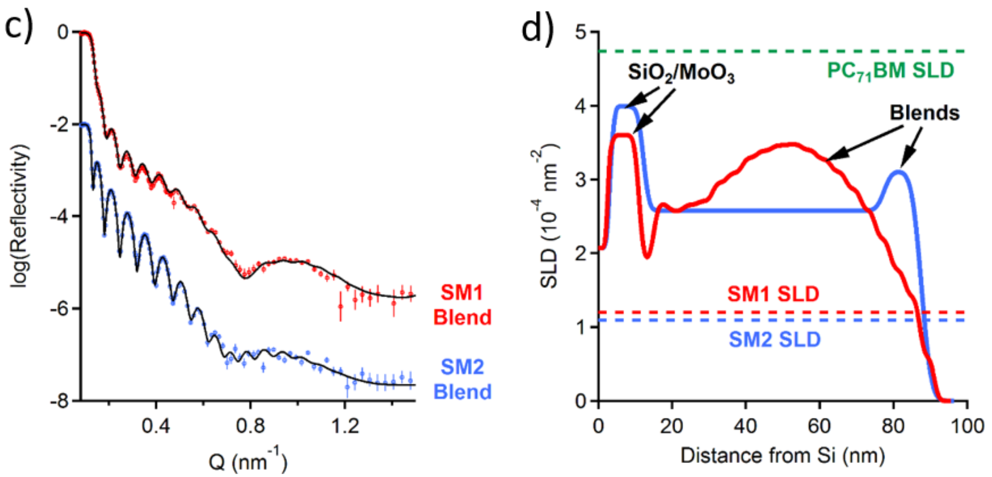
Always need model for accurate interpretation!
(Good to pair with microscopy)



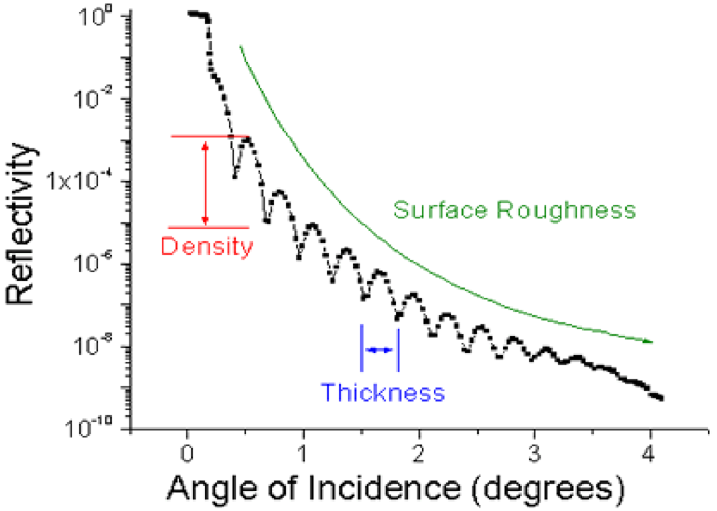
Reflectivity:
Nondestructive depth profile

- Resolution depends on q-range & "Kiessig" fringes (1-2 nm)
- <u>Software</u>: Motofit; Refl1D (NIST)



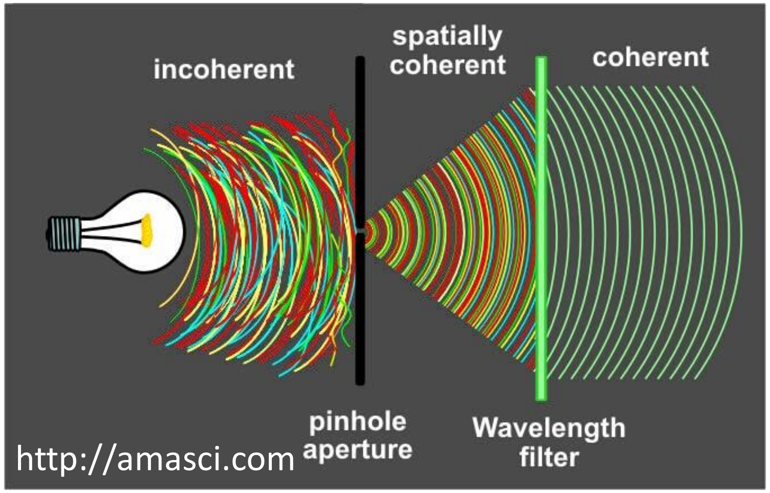


Alqhatani, *Adv Energ Mater*, (2018)

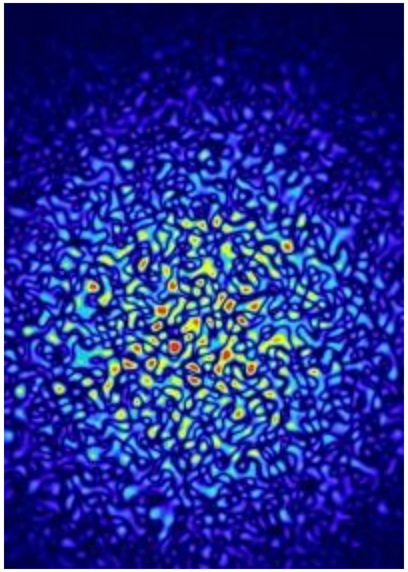


ALS ADVANCED LIGHT SOURCE

Coherent Scattering



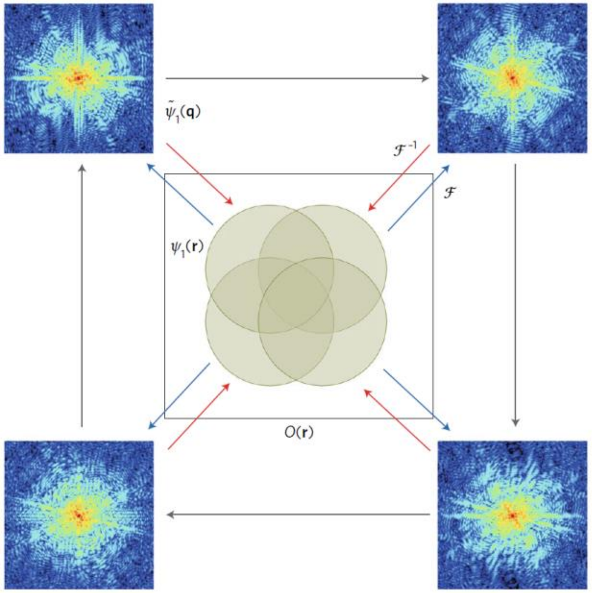
- Every source some coherence
  - Depends on source size, beam length, and spectral bandwidth
  - Make beam fully coherent via a pinhole the size of the coherence length
- When scattering, get ‘speckle patterns’ (complex interference pattern)
- Can use to ‘solve the phase problem’ to invert pattern into spatial image
  - “Coherent Diffractive Imaging” – ptychography
- Can monitor in time to capture dynamics
  - X-ray photocorrelation spectroscopy (XPCS)



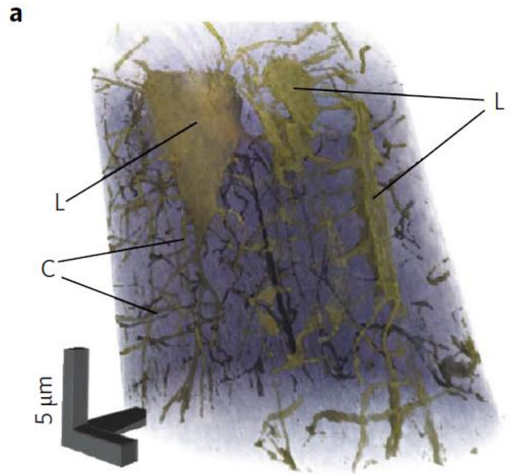
Shpyrko Group UCSD

Ptychography

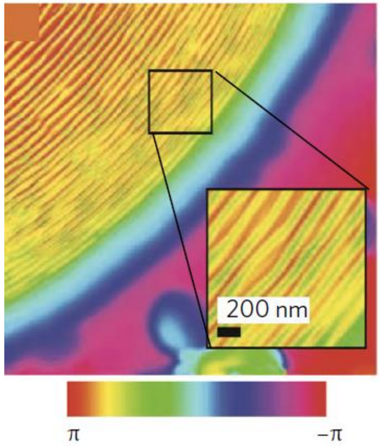
- Scattered wave is FFT of density distribution
$$A(\boldsymbol{q}) = FFT[\rho(\boldsymbol{r})]$$
- Measured intensities: Only the amplitudes!
$$I(\boldsymbol{q}) = A(\boldsymbol{q})A^*(\boldsymbol{q})$$
    - Can't take an inverse FFT to get $\rho(\boldsymbol{r})$ back!
- Coherent Diffractive Imaging recovers phase
    - CAN get $\rho(\boldsymbol{r})$ maps or even tomograms!
- Overlap coherent beam over sample
    - Diffraction limited microscopy



Pfeiffer, Nat Photon (2018)



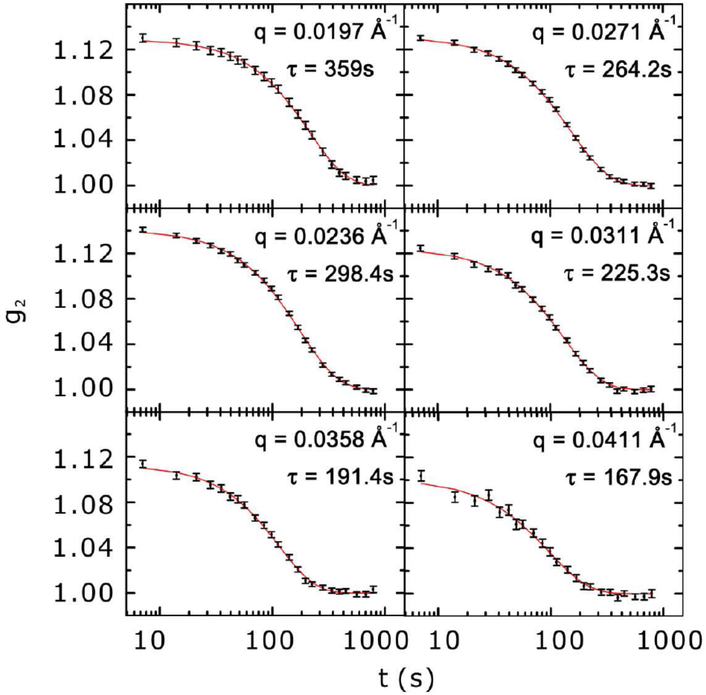
Dierolf, Nature, (2010)

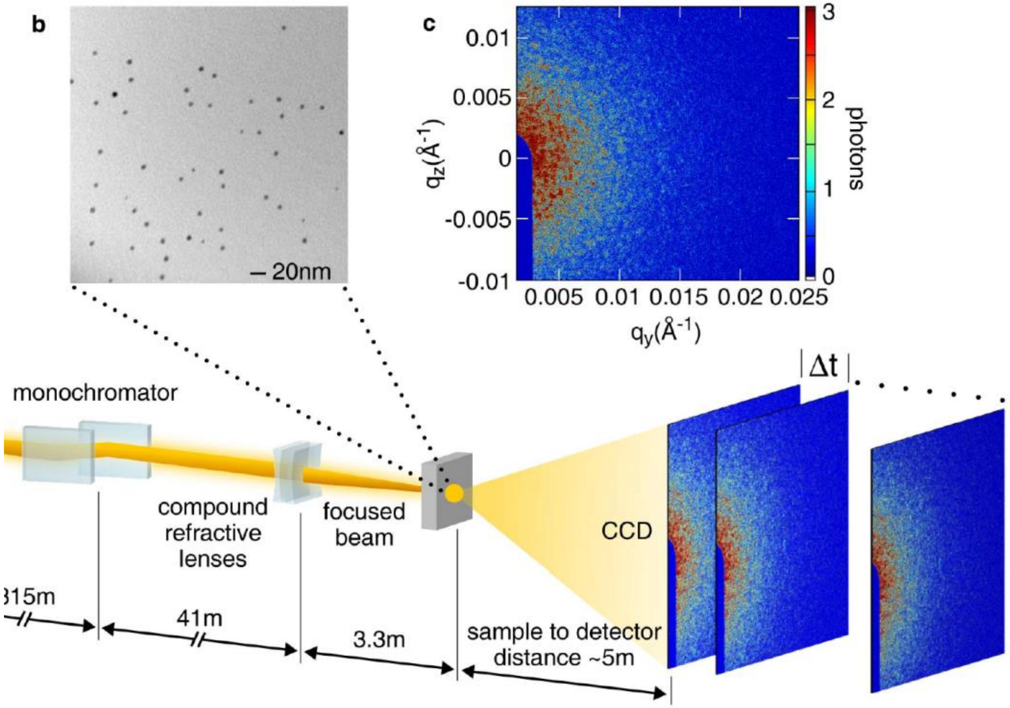


Thibault, *Science* (2008)

X-ray Photo Correlation Spectroscopy

Time scales of dynamic processes at the nano/atomic scale





Carnis, *Sci Rep* (2014)

Correlation functions at specific q-values for NPs in a polymer melt

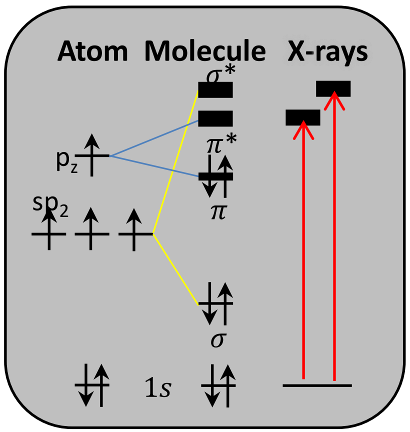
ALS ADVANCED LIGHT SOURCE

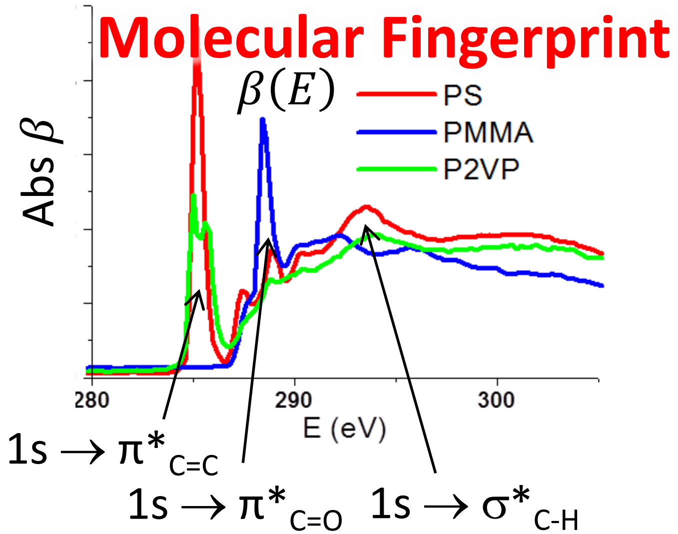
X-ray energy: New dimension in scattering

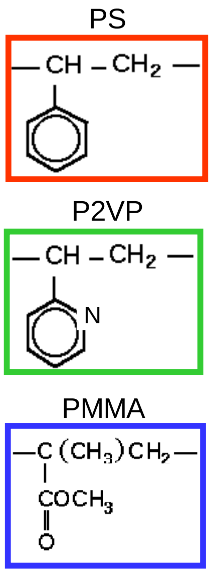
- Combine spectroscopy and scattering
  - Adds chemical information to structure measurement
- Elemental absorption edge (NEXAFS or XANES)
  - Organics: Carbon/Nitrogen/Oxygen – bond-sensitivity!
  - Metals: Fe/Co/Mn – oxidation & spin state sensitivity!

$$I(q) = \int \Delta\rho_e^2(r) e^{-iqr} \quad \rho_e = \frac{2\pi}{r_e \lambda} n$$

<u>Refr. Index</u>: $n(E) = 1 - \delta(E) + i\beta(E)$





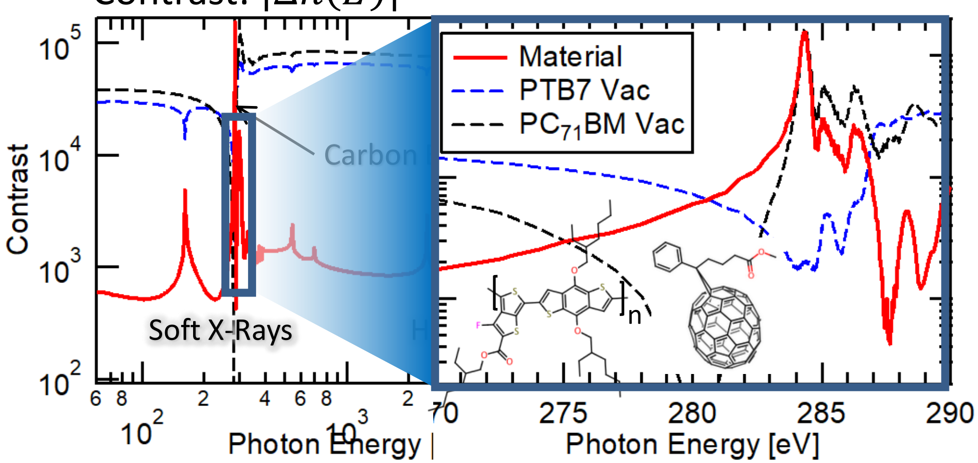


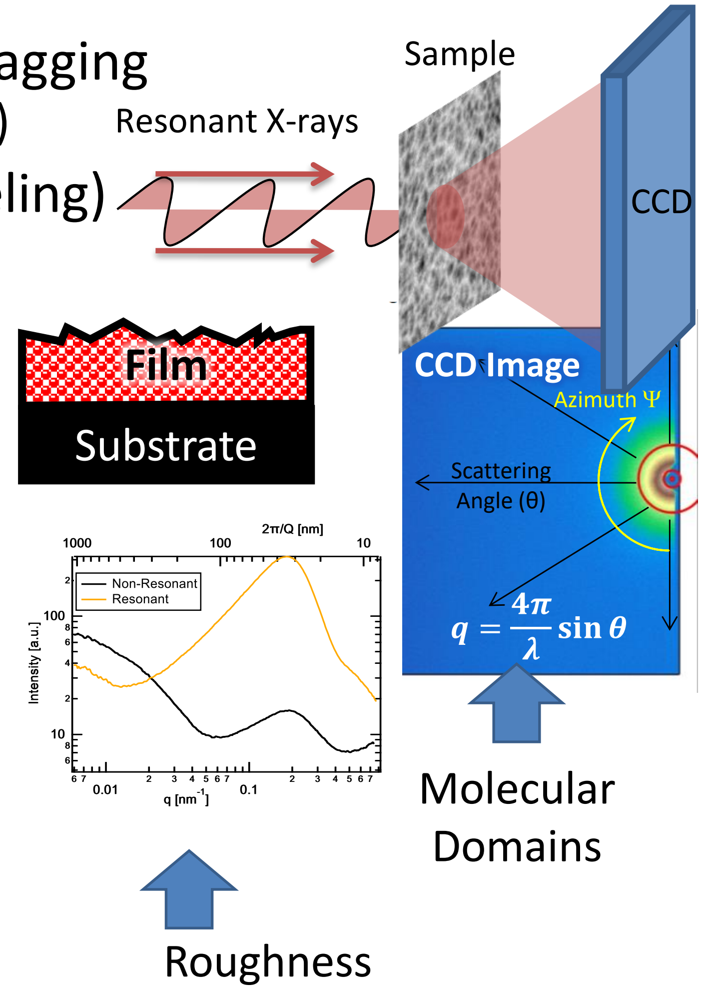
RSoXS: Bond-Sensitive Scattering

- Resonance: 100x better contrast, No Tagging
  - $I(E) \propto |\Delta\tilde{n}(E)|^2$ (n - index of refraction)
- Contrast variation (w/out isotopic labeling)
  - Non-resonant: roughness, porosity
  - Resonant: Material domains
- Domain compositions/purity from Total Scattering Intensity (TSI)

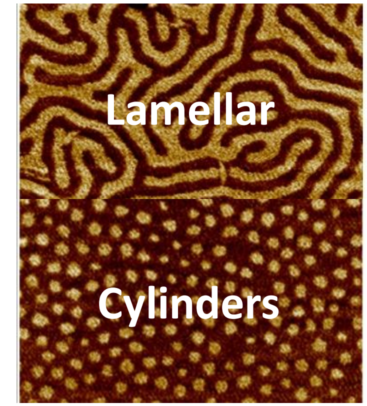
$$\mathrm{TSI} = \int_0^\infty I(q)q^2dq \propto \langle\Delta x\rangle^2$$

Contrast: $|\Delta n(E)|^2$



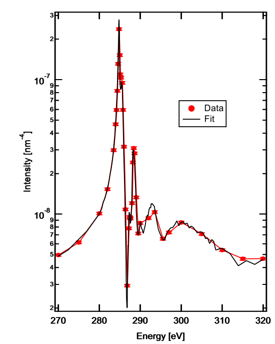


Measuring Nonplanar Interfaces



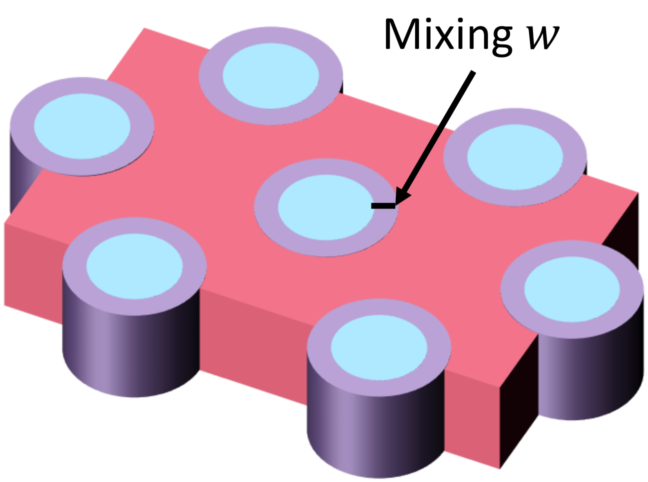
- Block copolymers have known morphologies
  - Thermo properties determines limits of nanostructure (energy cost of mixing)
  - Bottom-Up assembly for sub-10nm devices
  - Need to measure w
- Porod Invariant & Spectral Analysis

$$\underbrace{\int I(q,E)q^2dq}_{TSI(E)} = V|\Delta x_{12}|^2|\Delta n_{12}(E)|^2\left(\phi_1\phi_2 - \frac{1}{\sqrt{2}}\frac{S}{V}w\right)$$



$TSI(E)$

$\chi^2 = \mathbf{1.1}$



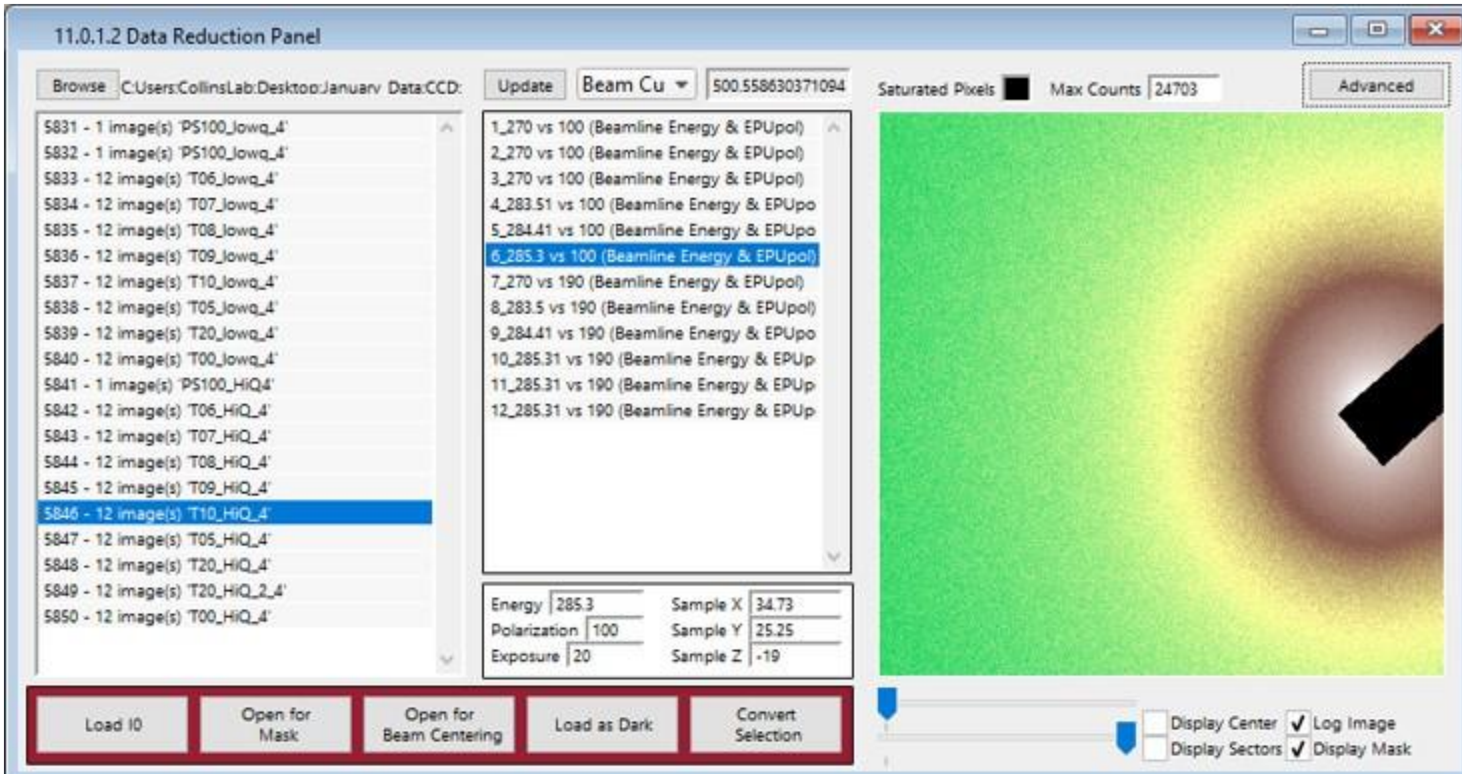
$w = 4.4 \pm 0.7nm$

1st measurement of non-planar interfaces in thin film!

Ferron *PRL* (2017)

RSoXS Data Processing Tool for 11.0.1.2

- Wrapper on NIKA to incorporate energy series into scattering experiments
- Download at Collins Website https://labs.wsu.edu/carbon/xray-analysis-tools/



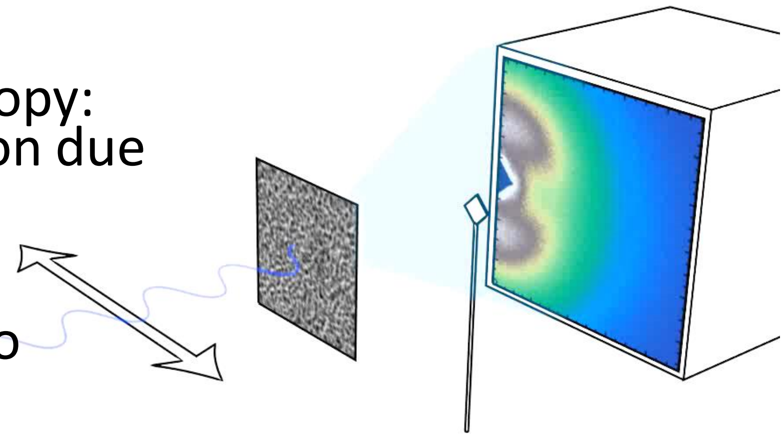
Polarized RSoXS: ***Spatially correlated orientation***

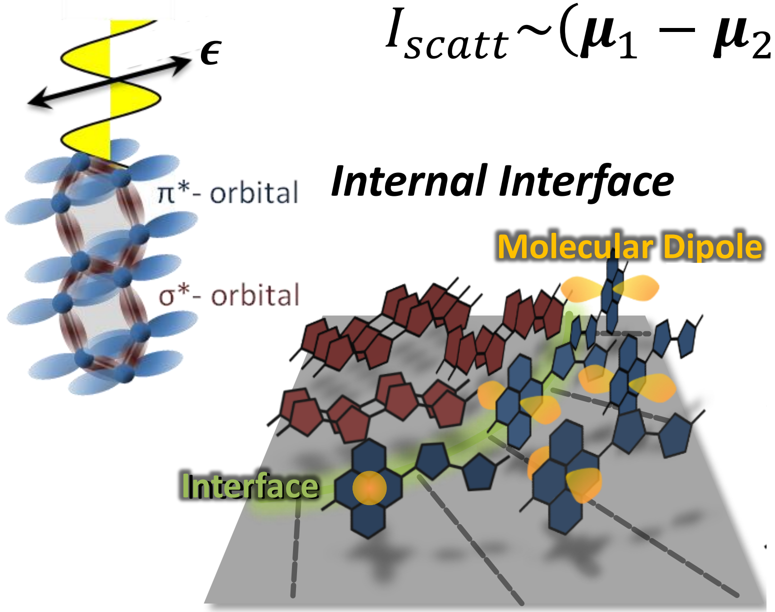
- Angle-dependent NEXAFS Spectroscopy: *sample average* molecular orientation due to transition dipole moment ($\boldsymbol{\mu}$)

$$I \sim \boldsymbol{\mu}_{avg} \cdot \boldsymbol{E}$$

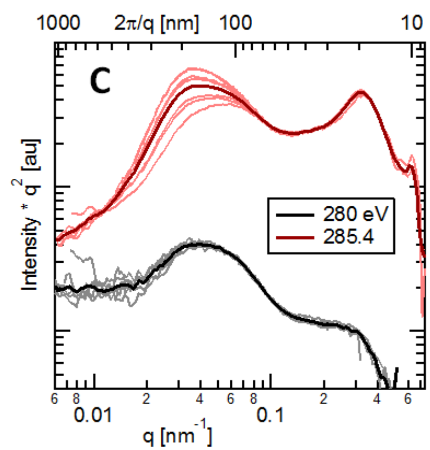
- Can use microscopy and scattering to measure ***local* orientation**

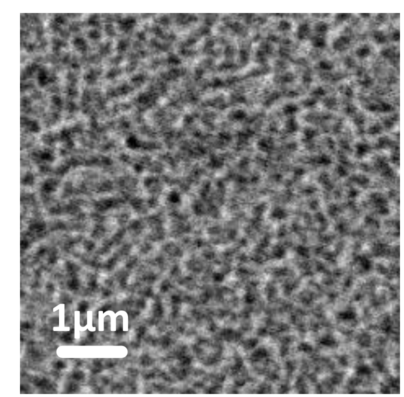
$$I_{scatt} \sim (\boldsymbol{\mu}_1 - \boldsymbol{\mu}_2) \cdot \boldsymbol{E}$$





Collins *et al.*, ***Nature Materials*** (2012).

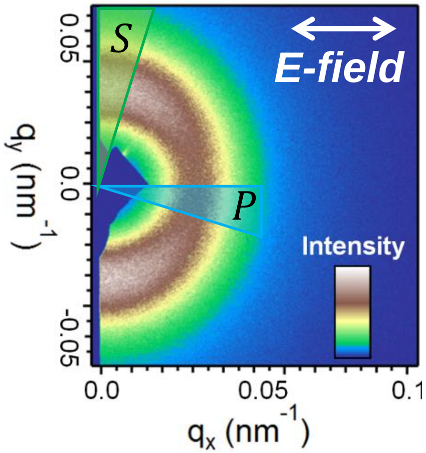


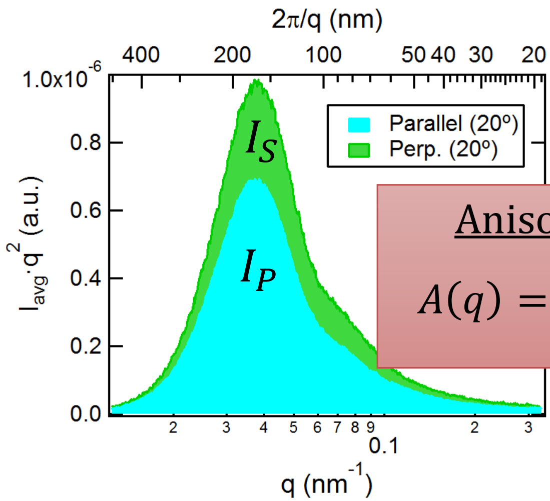


STXM: P3HT dark phase

Collins *et al.*, ***Nat. Mater.*** (2012).

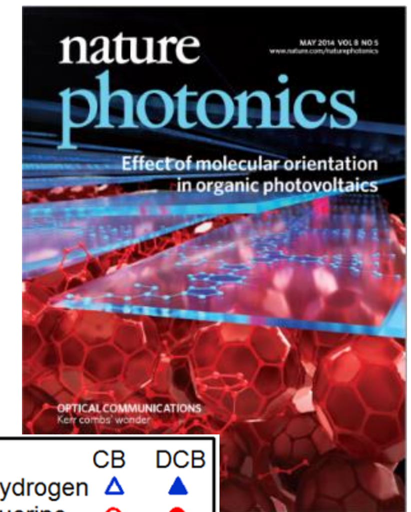
Quantifying Scattering Anisotropy

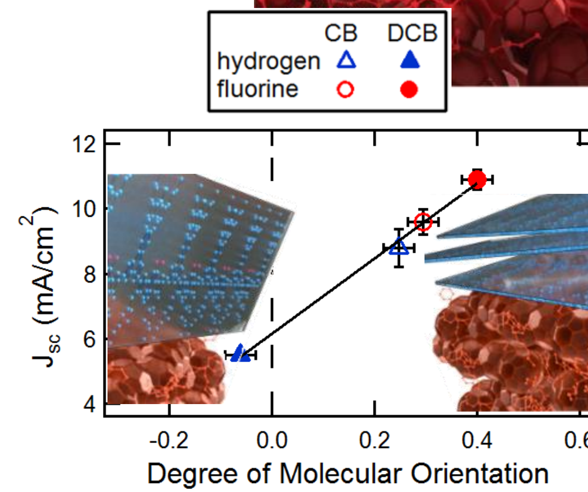




Anisotropy Ratio

$$A(q) = \frac{I_S(q) - I_P(q)}{I_S(q) + I_P(q)}$$



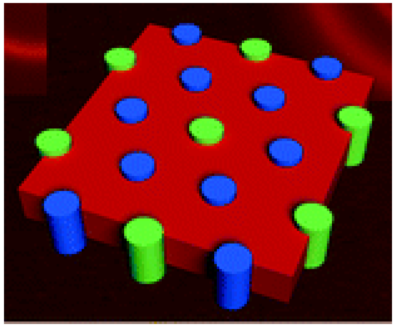


- Magnitude: Degree (statistics) of molecular ordering
- Sign: Preferred orientation in nanostructure

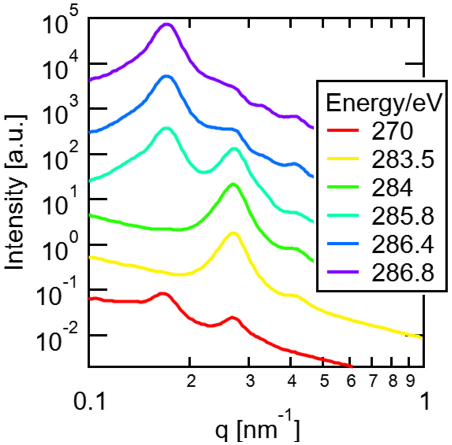
Tumbleston *et al.*, ***Nature Photon*** (2014).

RSoXS: High-Dimensional SAXS/SANS

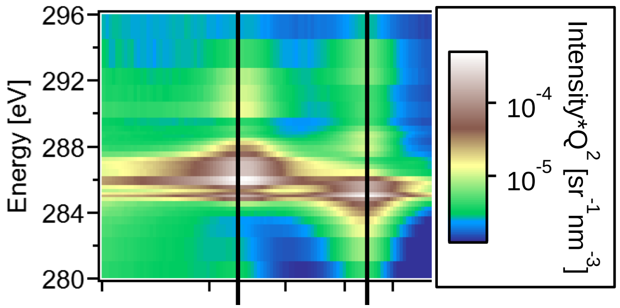
Deep characterization of molecular nanostructures



Wang et al, ***Nano Lett*** 2011

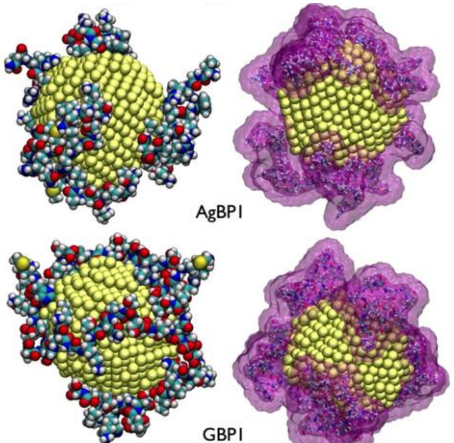


Chemical Ordering



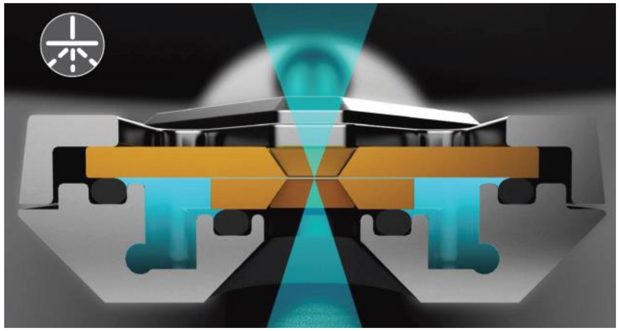
What about Solvated Nanostructures?!

Xu, *J of Drug Delivery* (2013).



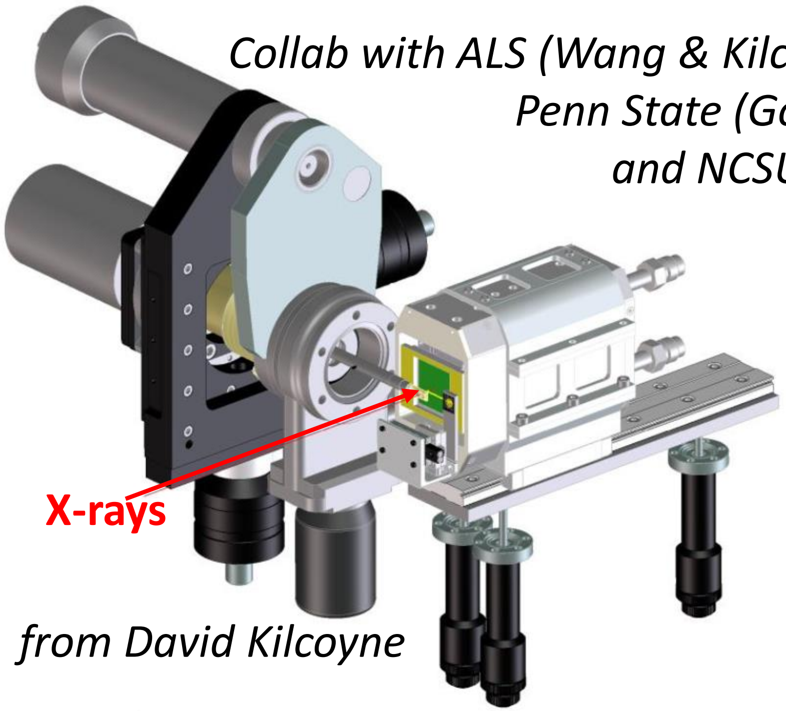
Walsh, *JACS* (2015)

Operando Environments

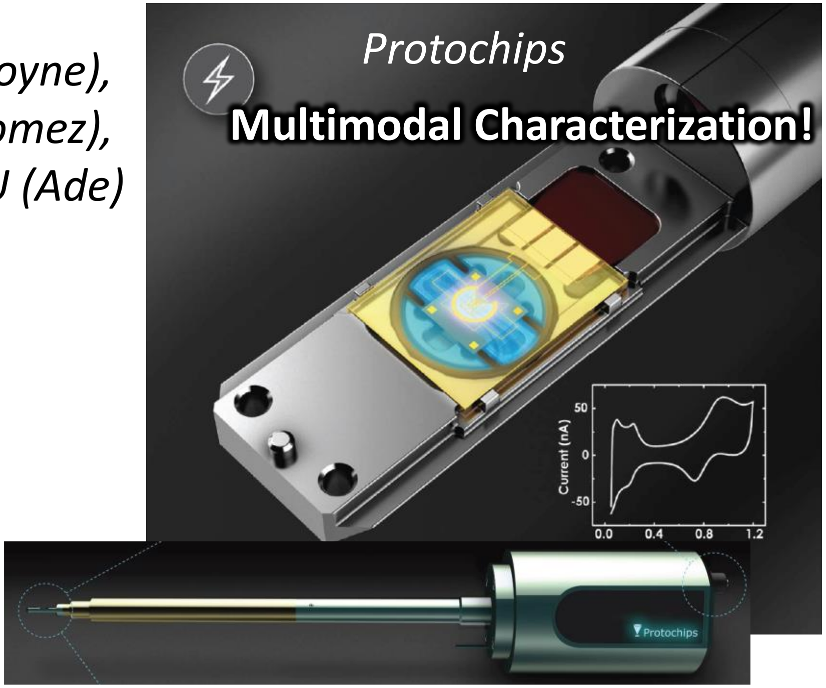


- Liquids, temperatures, electric fields
- TEM flow/electrochem cell by Protochips
  - Testing stage
- New RSoXS instrument designed by David Kilcoyne
  - Assembly and testing starting August

Collab with ALS (Wang & Kilcoyne), Penn State (Gomez), and NCSU (Ade)

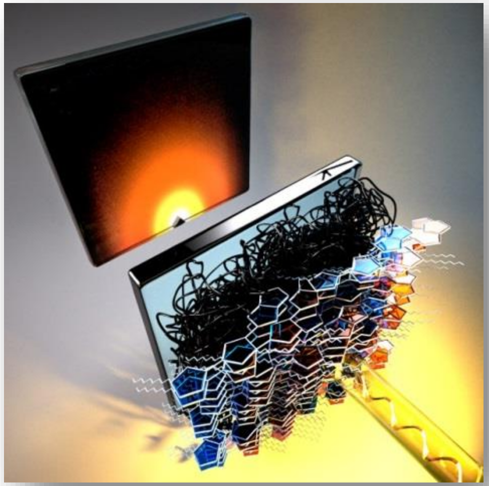


from David Kilcoyne

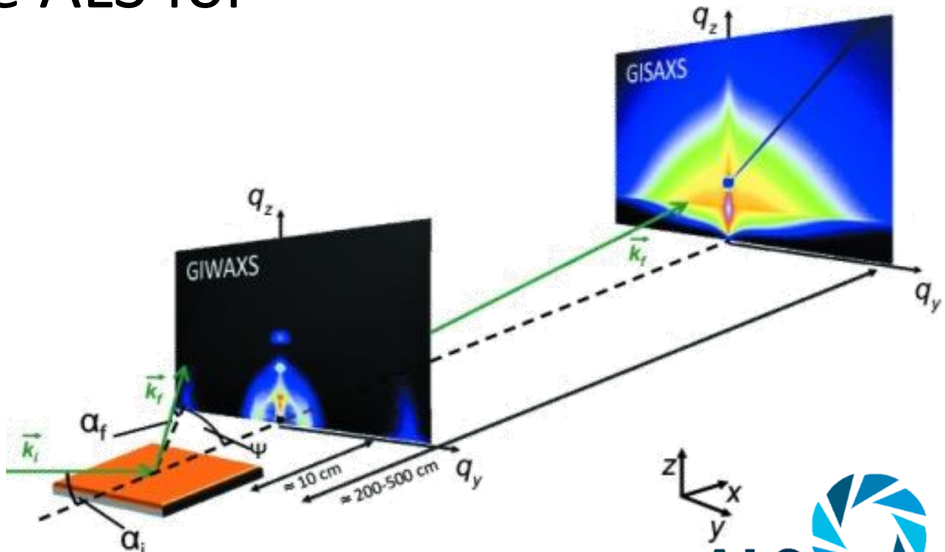


ALS ADVANCED LIGHT SOURCE

Summary

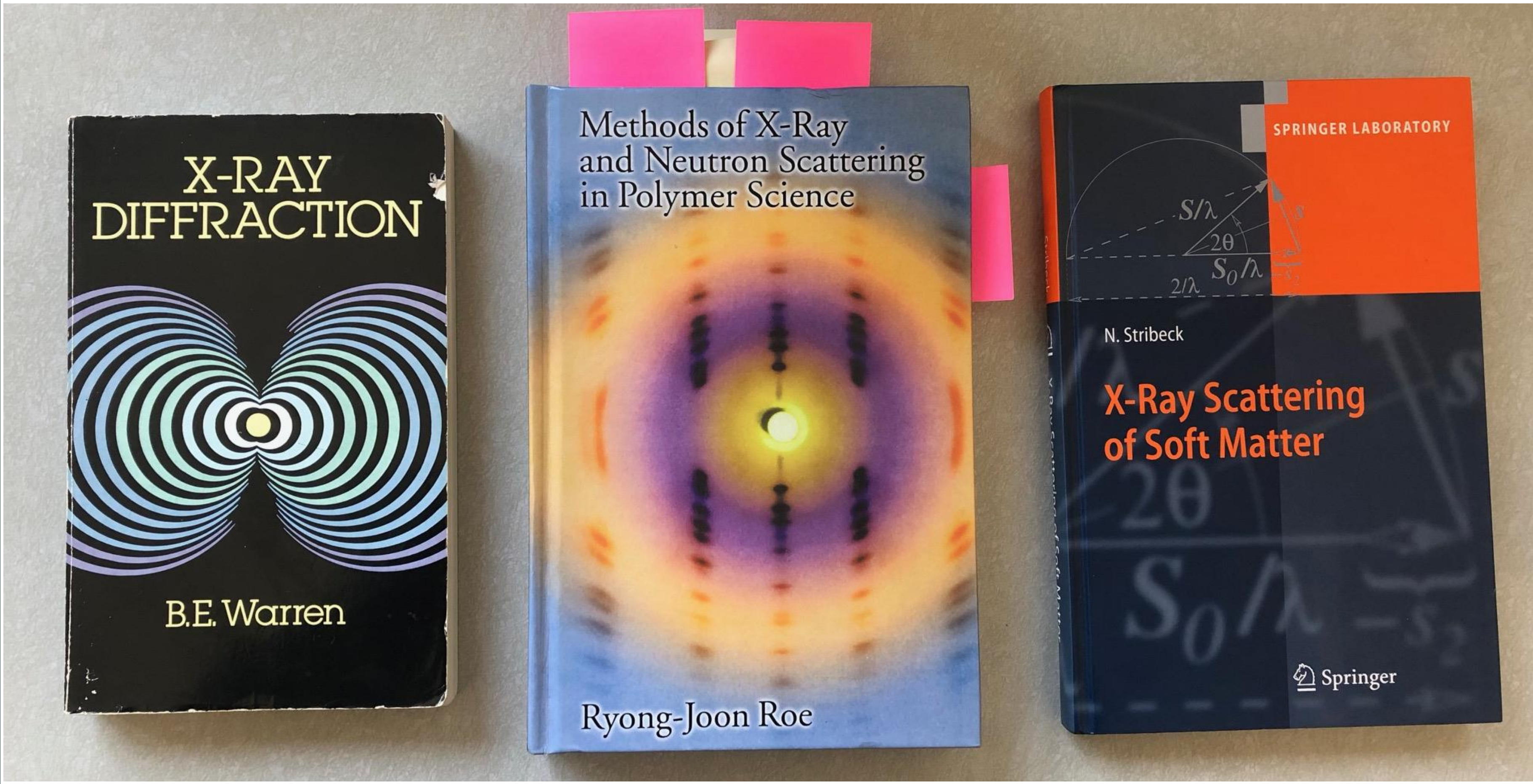


- Scattering reveals statistics of ordering
- Atomic –> nano –> micron sizescales
- Crystalline –> amorphous materials
- Inorganic –> organic –> biological materials
- Many opportunities at the ALS for scientists of all disciplines



ALS ADVANCED LIGHT SOURCE

Resources


X-RAY DIFFRACTION
B.E. Warren
Methods of X-Ray and Neutron Scattering in Polymer Science
Ryong-Joon Roe
SPRINGER LABORATORY
N. Stribeck
X-Ray Scattering of Soft Matter
Springer